SYNTHESIS AND SOME REACTIONS OF SELENOPHENO[2,3-c]PYRYLIUM SALTS

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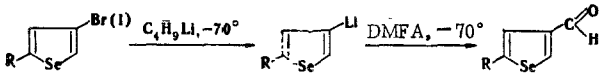
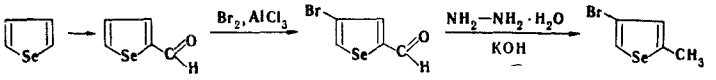
The catalytic acylation and subsequent heterocyclization of β-acetonyl derivatives of selenophene have been investigated. Methods have been proposed for the synthesis of new heteroaromatic systems: salts of the selenopheno[2,3-c]pyrylium cation and of selenopheno[2,3-c]pyridine. Methods have been developed for the synthesis of selenophene-3-carbaldehydes and 3-acetonylselenophenes.

In continuation of investigations on the synthesis of systems including condensed selenophene and pyrylium nuclei [1, 2], the present paper describes the synthesis of selenopheno[2,3-c]pyrylium salts and their reactions with ammonia, taking place with the formation of the corresponding selenopheno[2,3-c]-pyridines. A method has been developed for obtaining the initial β-acetonyl derivatives of selenophene by the reduction of the products of the condensation of aryl and hetaryl aldehydes with nitroethane [3, 4].

The initial selenophene-3-carbaldehyde and its 5-methyl and 5-ethyl derivatives were obtained with yields of 40-70% by the metallation of 3-iodoselenophene and 5-alkyl-3-bromoselenophenes with butyllithium at −70°C with the subsequent reaction of the resulting 3-lithioselenophene derivatives with dimethylformamide. An increase in the yield of aldehydes is brought about by the prolonged treatment of 3-iodoselenophene (30 min) and the 3-bromoselenophene derivatives (2 h) with the ethereal solution of butyllithium. This apparently shows that the replacement of the halogen atoms in the 3-halogeno derivatives by a metal takes place more slowly than in the thiophene series.



3-Iodoselenophene was obtained with a yield of 80% by the reduction of 2,3,4,5-tetraiodoselenophene [5] with zinc in acetic acid, and 3-bromo-5-methylselenophene by the Kishner [Wolff–Kishner] reduction of 3-bromoselenophene-5-carbaldehyde, which was synthesized by the bromination of the complex of selenophene-2-carbaldehyde with aluminum chloride [6].



3-Bromo-5-ethylselenophene was obtained similarly from 2-acetylselenophene. The individuality of the 3-bromo derivatives of selenophene synthesized was shown by gas–liquid chromatography. The selenophene-3-carbaldehydes [7] were isolated in the form of their derivatives – selenophen-3-ylmethylenebenzylamines:

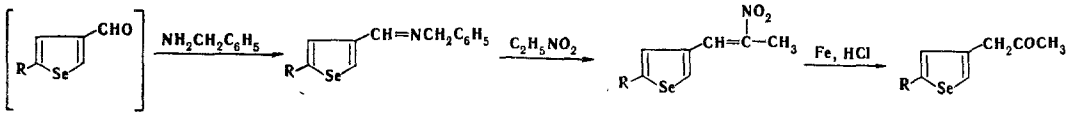


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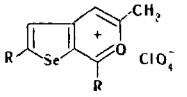
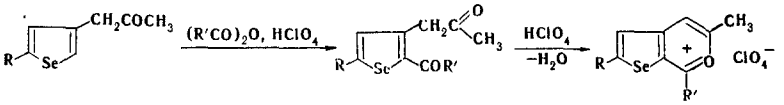
TABLE 1. Selenopheno[2,3-c]pyrylium Perchlorate

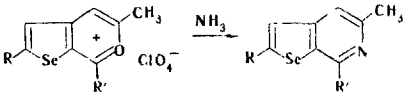


R	R′	Mp, °C	Empirical formula	Found, %				Calc., %				Yield, %
				C	H	Cl	Se	C	H	Cl	Se	
H	CH_3	176—177	$C_9H_9ClO_5Se$	34,9	3,0	11,5	25,2	34,7	2,9	11,4	25,4	77,3
H	C_2H_5	127—128	$C_{10}H_{11}ClO_5Se$	37,1	3,7	11,2	23,8	36,9	3,4	10,9	24,3	85,5
H	C_3H_7	104—105	$C_{11}H_{13}ClO_5Se$	39,1	4,0	10,7	23,0	38,9	3,8	10,5	23,3	68,0
CH_3	CH_3	172—173	$C_{10}H_{11}ClO_5Se$	37,0	3,5	11,1	24,1	36,9	3,4	10,9	24,3	82,6
CH_3	C_2H_5	133—134	$C_{11}H_{13}ClO_5Se$	39,0	3,9	10,3	23,1	38,9	3,8	10,5	23,3	85,7
CH_3	C_3H_7	120—121	$C_{12}H_{15}ClO_5Se$	40,8	4,4	10,3	22,3	40,7	4,2	10,0	22,3	93,2
C_2H_5	CH_3	182—183	$C_{11}H_{13}ClO_5Se$	38,7	4,1	10,6	23,0	38,9	3,8	10,5	23,3	78,8
C_2H_5	C_2H_5	129—130	$C_{12}H_{15}ClO_5Se$	41,0	4,4	10,3	22,1	40,7	4,2	10,0	22,3	76,5

The acylation of the ketones obtained with anhydrides of carboxylic acids in the presence of equimolecular amounts of perchloric acid led to the formation of diketones which, under the reaction conditions, underwent heterocyclization into selenopheno[2,3-c]pyrylium perchlorates, information on which is given in Table 1.



The acylation of 3-acetonylselenophene took place predominantly in the neighboring α position of the selenophene ring, as was shown by the formation of 4-acetonyl-2-acetylselenophene, the structure of which was confirmed by IR spectroscopy. Under the action of ammonia, the selenopheno[2,3-c]pyrylium perchlorates formed the previously unreported selenopheno[2,3-c]pyridines, the majority of which were identified in the form of the picrates and hydrochlorides (Table 2).



We have described other reactions of the selenopheno[2,3-c]pyrylium salts, leading to the formation of functional derivatives of benzoselenophene, elsewhere [8, 9].

EXPERIMENTAL

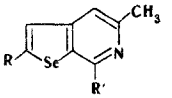
Gas–liquid chromatography was performed on a KhL-6 instrument (column 7.2 m long and 6 mm in diameter; stationary phase 0.4% of a copolymer of ethylene oxide and tetrahydrofuran on Inza brick, 60-80 mesh fraction; carrier gas helium, rate of flow 3 liters/min; column temperature 150°C).

The individuality of the β-acetonylselenophenes and of the selenopheno[2,3-c]pyridines was checked by thin-layer chromatography on alumina of activity grade II in the benzene–chloroform–hexane–acetone (30 : 6 : 1 : 4) system, the spots being revealed with iodine vapor in ultraviolet light.

Selenophene-2-carbaldehyde was synthesized by the formylation of selenophene by the Vilsmeier reaction [10].

4-Bromoselenophene-2-carbaldehyde. With vigorous stirring, 47.7 g (0.3 mole) of selenophene-2-carbaldehyde was added over 5 min to 100 g (0.75 mole) of anhydrous $AlCl_3$ (at a temperature not exceeding 50°C), and then 18 ml (0.36 mole) of bromine was rapidly added dropwise; the mixture was stirred for 10 min and was poured into a mixture of 500 g of ice and 90 ml of hydrochloric acid. The precipitate was extracted with ether and the extract was washed with sodium carbonate solution and with water and was dried with sodium sulfate. The ether was distilled off and the residue was recrystallized. Yield 43.5 g (61%). Mp 87°C (from hexane; yellowish-pink needles). Found, %: C 25.4; H 1.4; Br 33.4; Se 33.0. C_5H_3BrOSe. Calculated, %: C 25.2; H 1.3; Br 33.6; Se 33.2. Semicarbazone, mp 237-238°C (from ethanol). Found, %: C 24.6; H 2.1; Br 27.0; N 14.4. $C_6H_6BrN_3OSe$. Calculated, %: C 24.4; H 2.0; Br 27.1; N 14.2.

TABLE 2. Selenopheno[2,3-c]pyridines



R	R′	Picrate			
		mp, °C	empirical formula	N, % found	N, % calc.
H	CH_3	162—163	$C_9H_9NSe \cdot C_6H_3N_3O_7$	12,6	12,7
H	CH_3*	318—320	$C_9H_9NSe \cdot HCl$	5,6	5,7
H	C_2H_5	161—162	$C_{10}H_{11}NSe \cdot C_6H_3N_3O_7$	12,3	12,4
H	C_3H_7	155—156	$C_{11}H_{13}NSe \cdot C_6H_3N_3O_7$	12,1	12,0
CH_3	CH_3	208—209	$C_{10}H_{11}NSe \cdot C_6H_3N_3O_7$	12,5	12,4
CH_3	CH_3*	>300	$C_{10}H_{11}NSe \cdot HCl$	5,5	5,4
CH_3	C_2H_5	190—191	$C_{11}H_{13}NSe \cdot C_6H_3N_3O_7$	11,8	12,0
CH_3	C_3H_7	148—149	$C_{12}H_{15}NSe \cdot C_6H_3N_3O_7$	11,8	11,6
C_2H_5	CH_3	153—154	$C_{11}H_{13}NSe \cdot C_6H_3N_3O_7$	12,2	12,0
C_2H_5	C_2H_5	139—140	$C_{12}H_{15}NSe \cdot C_6H_3N_3O_7$	11,8	11,6

* The figures for the hydrochloride are given.

4-Bromo-2-methylselenophene. With stirring, a mixture of 119 g (0.5 mole) of 4-bromoselenophene-2-carbaldehyde and 300 ml of diethylene glycol was added to a mixture of 100 ml of hydrazine hydrate and 200 ml of diethyleneglycol over 30 min, and the mixture was heated on the boiling water bath for 10 min, cooled, and transferred to a 2-liter flask, and then 84 g (1.5 mole) of caustic soda was added and a distillate was taken off up to 160°C. The distillate was acidified with 10% hydrochloric acid to pH 3-5, the organic layer was extracted with ether, and the extract was washed with water and dried with sodium sulfate. After the ether had been evaporated off, the residue was distilled in vacuum. Yield 73.3 g (65.8%). Bp 67-69°C (4 mm). Found, %: C 27.0; H 2.4; Br 36.0; Se 35.0. C_5H_5BrSe. Calculated, %: C 26.8; H 2.2; Br 35.7; Se 35.3.

2-Methylselenophen-4-ylmethylenebenzylamine. In a current of nitrogen, a solution of 33.7 g (0.15 mole) of 4-bromo-2-methylselenophene in 200 ml of absolute ether cooled to −70°C was added to an ethereal solution of n-butyllithium (from 3.4 g of lithium) also at −70°C, and the mixture was stirred for 2 h and was then added with stirring to a solution of 21.9 g (0.3 mole) of dimethylformamide in 200 ml of absolute ether also cooled to −70°C. The resulting mixture was stirred for another 2 h and was left overnight. Then it was poured onto ice, and the ethereal layer was separated off, washed with water, and dried with calcium chloride. The solvent was evaporated off and the residue was distilled in vacuum, a fraction with bp 50-85°C (3-4 mm) being collected. This fraction was treated with a solution of 18 ml of benzylamine in 50 ml of benzene and the mixture was boiled for 10 min, after which the benzene and the excess of benzylamine and the unchanged 4-bromo-2-methylselenophene were driven off in vacuum on a boiling water bath. The residue was distilled in vacuum. Yield 25.3 g (65.6%) of 2-methylselenophen-4-ylmethylenebenzylamine, bp 174-176°C (4 mm). Found, %: C 59.8; H 5.1; N 5.2. $C_{13}H_{13}NSe$. Calculated, %: C 59.5; H 4.9; N 5.3.

1-(5-Methylselenophen-3-yl)-2-nitropropylene. A mixture of 25 g (0.1 mole) of 5-methyl-3-selenophenylmethylenebenzylamine and 7.5 g (0.1 mole) of nitroethane in 30 ml of acetic acid was heated in the boiling water bath for 5 min and was then cooled, and the yellow precipitate was filtered off, washed with water and with ethanol, and dried. This gave 16 g of product. The addition of 100 ml of water to the filtrate yielded another 4 g. Total yield 20 g (88.3%). Mp 52°C (from ethanol). Found, %: N 6.2. $C_8H_9NO_2Se$. Calculated, %: N 6.1.

3-Acetonyl-5-methylselenophene. Over 2 h, 35 ml of concentrated hydrochloric acid was added to a mixture of 19.9 g (0.087 mole) of 1-(5-methylselenophen-3-yl)-2-nitropropylene, 20 ml of toluene, 25 g of iron, 0.5 g of ferric chloride, and 50 ml of water, and the resulting mixture was boiled with stirring for another 30 min and was distilled with steam. The organic layer was separated off and the aqueous layer was extracted with chloroform. After the elimination of the solvents, the residue was distilled in vacuum. Yield 10.6 g (60.6%). Bp 83-85°C (3 mm). R_f 0.86. Found, %: C 47.9; H 5.1; Se 39.1. $C_8H_{10}OSe$. Calculated, %: C 47.8; H 5.0; Se 39.3. IR spectrum: 1723 cm^{-1}. Semicarbazone, mp 149-150°C (from ethanol). Found, %: N 16.4. $C_9H_{13}N_3OSe$. Calculated, %: N 16.3.

2-Acetyl-4-bromoselenophene was obtained from 2-acetylselenophene [11] by the method described for the synthesis of 4-bromoselenophene-2-carbaldehyde. Yield 53.5%. Mp 73-74°C (from hexane). Found,

%: C 28.8; H 2.2; Br 31.5; Se 31.1. C_6H_5BrOSe. Calculated, %: C 28.6; H 2.0; Br 31.7; Se 31.3. Semicarbazone, mp 266-267°C (from ethanol). Found, %: N 13.5. $C_7H_8BrN_3OSe$. Calculated, %: N 13.6.

4-Bromo-2-ethylselenophene was obtained from 2-acetyl-4-bromoselenophene by the method described for the synthesis of 4-bromo-2-methylselenophene. Yield 63.0%. Bp 72-73°C (5 mm). Found, %: C 30.5; H 3.2; Br 33.4; Se 32.9. C_6H_7BrSe. Calculated, %: C 30.3; H 3.0; Br 33.6; Se 33.1.

2-Ethylselenophen-4-ylmethylenebenzylamine was obtained from 4-bromo-2-ethylselenophene by the method described for the synthesis of 2-methyl-4-selenophenylmethylenebenzylamine. Yield 37.7%. Bp 181-185°C (4 mm). Found, %: C 61.0; H 5.7; N 5.0. $C_{14}H_{15}NSe$. Calculated, %: C 60.9; H 5.4; N 5.1.

1-(2-Ethylselenophen-4-yl)-2-nitropropylene was obtained from 2-ethyl-4-selenophenylmethylenebenzylamine by the method described for the synthesis of 1-(2-methylselenophen-4-yl)-2-nitropropylene. Oily liquid. The product was used without purification for reduction to 4-acetonyl-2-methylselenophene.

3-Acetonyl-5-ethylselenophene was obtained from 1-(2-ethylselenophen-4-yl)-2-nitropropylene by the method described for the synthesis of 3-acetonyl-5-methylselenophene. Yield 32.6%. Bp 100-103°C (4 mm). R_f 0.82. Found, %: C 50.5; H 5.4; Se 36.7. $C_9H_{12}OSe$. Calculated, %: C 50.2; H 5.6; Se 36.9. IR spectrum: 1724 cm^{-1}. Semicarbazone, mp 109-110°C (from aqueous ethanol). Found, %: N 15.3. $C_{10}H_{15}N_3OSe$. Calculated, %: N 15.4.

3-Iodoselenophene. A mixture of 95.3 g (0.15 mole) of 2,3,4,5-tetraiodoselenophene [5], 30 ml of acetic acid, and 100 ml of water was treated with 60 g of zinc dust and boiled for 30 min. The reaction mixture was distilled with steam until 600 ml of distillate had been collected, and this was neutralized with potassium carbonate solution. The organic layer was separated off, the aqueous layer was extracted with ether, and the extract was dried with calcium chloride. The solvent was evaporated off and the residue was distilled in vacuum. Yield 31.1 g (80.7%). Bp 59-61°C (2 mm). Found, %: C 18.9; H 1.1; I 49.3; Se 30.6. C_4H_3ISe. Calculated, %: C 18.7; H 1.2; I 49.4; Se 30.8.

Selenophen-3-ylmethylenebenzylamine was obtained from 3-iodoselenophene by the method described for the synthesis of 2-methyl-4-selenophenylmethylenebenzylamine. After the addition of the 3-iodoselenophene to the n-butyllithium, the reaction mixture was stirred for 30 min. Yield 60%. Bp 163-164°C (3 mm). Found, %: C 58.2; H 4.6; N 5.5. $C_{12}H_{11}NSe$. Calculated, %: C 58.1; H 4.4; N 5.6.

1-(Selenophen-3-yl)-2-nitropropylene was obtained from 3-selenophenylmethylenebenzylamine by the method described for the synthesis of 1-(5-methyl-3-selenophenyl)-2-nitropropylene. Yield 83.5%. Mp 68-69°C (from ethanol). Found, %: N 6.3. $C_7H_7NO_2Se$. Calculated, %: N 6.5.

3-Acetonylselenophene was obtained from 1-(3-selenophenyl)-2-nitropropylene by the method described for the synthesis of 4-acetonyl-2-methylselenophene. Yield 64%. Bp 81-83°C (3 mm). R_f 0.85. Found, %: C 45.0; H 4.4; Se 42.1. C_7H_8OSe. Calculated, %: C 44.9; H 4.3; Se 42.3. IR spectrum: 1723 cm^{-1}. Semicarbazone, mp 152-153°C (from aqueous ethanol). Found, %: N 17.3. $C_8H_{11}N_3OSe$. Calculated, %: N 17.2.

2,5,7-Trimethylselenopheno[2,3-c]pyrylium Perchlorate. With stirring, a mixture of 12.5 ml (0.125 mole) of acetic anhydride and 2 ml (0.025 mole) of 70% perchloric acid cooled with ice water was added to 5.03 g (0.025 mole) of 3-acetonyl-5-methylselenophene, and the mixture was left for 30 min, after which 50 ml of ether was added and the precipitate was filtered off and washed with ether. The other selenopheno[2,3-c]pyrylium perchlorates (Table 1) were obtained similarly.

4-Acetonyl-2-acetylselenophene. The ethereal solution after the isolation of the 5,7-dimethylselenopheno[2,3-c]pyrylium perchlorate was washed with sodium carbonate solution and with water and was dried with calcium chloride. After the solvent had been driven off, an oily liquid was obtained which did not crystallize when it was cooled with ice. IR spectrum: 1728, 1673 cm^{-1}. Disemicarbazone, mp 215-217°C (from aqueous ethanol). Found, %: C 39.2; H 5.0; N 24.2; Se 22.7. $C_{11}H_{16}N_6O_2Se$. Calculated, %: C 38.8; H 4.7; N 24.5; Se 23.0.

5,7-Dimethylselenopheno[2,3-c]pyridine. Ammonia was passed for 15 min into a mixture of 3.11 g (0.01 mole) of 5,7-dimethylselenopheno[2,3-c]pyrylium perchlorate and 35 ml of ethanol, and the mixture was boiled for 15 min and poured into 100 ml of water. The organic layer was separated off and the aqueous layer was extracted with ether, and then the extract was washed with water and dried with caustic potash. After the solvent had been distilled off, the product solidified. Yield 1.67 g (80%). Mp 42°C (from hexane). Found, %: C 51.7; H 4.5; N 6.4; Se 37.3. C_9H_9NSe. Calculated, %: C 51.4; H 4.3; N 6.7; Se 37.6.

The other selenopheno[2,3-c]pyridines were obtained similarly; details of them are given in Table 2.

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